

Capacity Losses During Thermal Storage of Graphite Lithium Anode

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Using prototype lithium ion batteries, a recent study carried out by the SAFT group [1] showed that the major contribution to self-discharge is anode corrosion. However more specific anode study requires the use of Li/ electrolyte/graphite half-cells with internal reference. We have conducted such a study and published preliminary results based on combined galvanostatic cycling and EIS measurements [2]. In this study, two or three electrode Li/electrolyte/graphite coins cells were constructed using an in house technique [3]. The working electrode composition was 75PCUK) and 15 were subjected to 10-15 first cycles under C/5 rate, between 1.5V and 0V vs. Li to determine the initial capacity $Q_{rev}(0)$. The final operation consisted of a cell discharge down to 0 mV vs. Li, for which the graphite composition is closed to LiC_6 (full lithiation). Cells were then stored at open-circuit at 70 °C for periods of 1, 2, 3, 4 and 8 days, then were charged to 1.5 V to determine the remaining capacity $Q_{rem}(t)$. This was followed by 10 cycles to determine the new reversible capacity, $Q_{rev}(t)$. EIS measurements were performed at the end of the first cycles at the charged state and after thermal storage. The $\log Q_{rem}(t)/Q_{rev}(0)$ vs. time curve shows a linear behavior, indicating a first order kinetic law : $Q_{rem}(t)=Q_{rev}(0).\exp(-lt)$. The discharge kinetic constant was found $l=0.17$ day⁻¹. This translates into a cell half- life close to 4 days at 70°C. Analysis of the EIS spectra shows that electrolyte resistance increased by 100 by nearly 400 days. A similar behavior is observed with the charge transfer resistance. Concomitantly the film and the double layer capacitance gradually decreased. This suggests two reverse effects, one leading to increased resistances such new species precipitation to form the SEI, and another decreasing the resistances as a likely result of a partial SEI dissolution. The observed decreased capacitance should be associated with decreased active surface area of the electrode as result of increased amounts of the isolating components of the SEI, i.e. LiF and Li_2CO_3 . XRD performed on the graphite electrode before and after storage indicated no significant structural changes, in particular, no solvent co-intercalation or graphite exfoliation. Therefore, the capacity loss is mainly due to surface effects. The metastable adsorbed complex model To cope with the observed phenomena, we propose the formation of a metastable electron-ion-electrolyte complex that adsorbs on the graphene edges. Intercalated lithium ions tends to diffuse to under the chemical potential created by adsorbed PF_6^- and solvent molecules leading to the complex formation. Such a complexe is metastable in the sense that during the electrode delithiation (cell

charge) after storage, the electron would not be used to accompany the lithium de-intercalation and therefore would account for the total capacity loss. On the other hand, it is unstable since under thermal activation, a part of the adsorbed electron would transfer to the electrolyte (reduction of PF_6^- , EC, DMC, impurities), which would result in LiF , Li_2CO_3 , and other lithium alkyl-carbonates or polymer formation [4]. Such chemical reduction is irreversible in nature and would account for the irreversible capacity loss. This model diverges from that proposed by the Saft group model [1] who assumed a shuttle mechanism of dissolved species to deal with the self- discharge phenomena. Though their model could be acceptable in a complete lithium-ion

cell, it cannot apply in the case of a half cell which contains two "anode- type" electrodes; lithiated graphite and lithium having very close potentials.

References: [1] M. Broussely et al. Proc. 10 IMLB, Como, Italy, 2000. To appear in J. Power Sources 2001 [2] R. Yazami in Materials for Lithium-Ion Batteries, Kluwer Aca. Publ. (2000)105 [3] A. Martinent et al. Proc. 10 IMLB, Como, Italy, 2000. To appear in J. Power Sources 2001 [4] S. Genies et al. Synthetic Metals 93(1998)286